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GEOCHEMISTRY OF FGD WASTE BY-PRODUCTS

Report No 88-329-K

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Abstract

A laboratory study was undertaken to define and evaluate the properties of flue gas desulphurization (FGD) waste by-products in terms of their chemical characteristics, leaching behaviour, and leachate interactions with clay liner materials. Specifically, the test materials used in this study are based on the limestone/lime injection into the furnace (LIF) process evaluation test runs carried out at Lakeview TGS.

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GEOCHEMISTRY OF FGD WASTE BY-PRODUCTS

1.0 INTRODUCTION

Flue gas desulphurization (FGD) is developing as a viable technology to control acid gas emissions from coal-fired generating stations. As part of the overall Ontario government effort to reduce acid gas emissions, Ontario Hydro is evaluating SO_x control by injection of pulverized limestone directly into the furnace (LIF) at one of its coal fired thermal generating stations at Lakeview TGS Unit 4 and 5 (Mozes et al., 1988). Although the efficiency of SO_x removal by this process is relatively low (~50%) compared to other available processes, LIF does have the advantage of being the most adaptable in terms of installation and retrofitting at existing coal-fired generating stations. However, the LIF process does generate a considerable amount of waste by-products which will have to be disposed of.

The disposal of LIF by-products in either a landfill or pit/quarry operation will require the assessment of the long-term environmental impact of the leachate generated. To date little is known regarding the long-term environmental impact of leaching characteristics of FGD waste material or its potential effect on the physical and hydraulic properties of liner/overburden materials placed in direct contact with it.

In order to develop an adequate data base on FGD waste by-products, a geochemical study has been initiated in the Civil Research Department with particular reference to the establishment of the following FGD waste characteristics:

(a) chemical and mineralogical composition.

(b) leaching behaviour and evolution of leachate chemistry with time.

(c) nature and extent of geochemical interactions between FGD leachate and clay liner materials.

In this report, the results of FGD waste characterization and the leaching tests are presented. A preliminary interpretation of FGD leachate data using the geochemical computer program PHREEQE is presented, emphasizing FGD leachate/clay liner interactions and their relevance to FGD waste disposal.

2.0 MATERIALS

The FGD waste materials used in the study were generated at Lakeview TGS as part of the LIF process evaluation test runs in July/August, 1987. Three different LIF samples, designated as LIF-1, LIF-2, and LIF-3, were obtained for the characterization study. Specifically, LIF-1 and LIF-2 are waste by-products generated from the limestone ($CaCO_3$) process, whereas LIF-3 is based on the lime process. The same test materials have been used in the FGD by-product mine backfill study (Chan et al., 1988).

3.0 LIF WASTE CHARACTERIZATION

3.1 Slaking Tests and Determination of Exothermicity

Slaking tests are performed on test materials using a procedure recommended by Ms. P. Williams of the Chemical Research Department. Briefly, the procedure involves addition of water incrementally (1.5x the CaO content of waste material) to the test sample. The slaking process is accompanied by evolution of heat, yielding a dry, powdery product. The second step in the slaking process involves further addition of water (28% of the mass of pre-slaked material) to produce a water-saturated, moist product which is suitable for transportation to a disposal site. The amount of water added in the slaking process and the observed increase in the mass of the test material as a result of slaking are presented in Table 3.1.

The net mass increase following slaking is less than the total amount of water added in the slaking process. This can be attributed to the loss of moisture by evaporation, a result of the exothermic nature of the reaction occurring during slaking. In the following sections, unslaked material will be designated as "as received" and material subjected to the slaking process as "slaked".

The heats of reaction of the test materials were determined using a calorimetric method described by Golomb (1987). The exothermicity data are presented in Table 3.2. The heat of reaction (ΔH) can also be calculated, assuming that all free lime reacts with water to form slaked lime (portlandite).

$$CaO + H_2O = Ca(OH)_2 \qquad (1)$$

ΔH for the reaction is -65.08 KJ (-278 cal/g).

TABLE 3.1

SLAKING RESULTS OF LIF WASTE MATERIALS

	Mass (g)		
	LIF-1	LIF-2	LIF-3
Amount of Waste Material Used	1000	1000	1000
Total Amount of Water Added	443	440	443
Mass of Slaked Material	1376	1385	1374
Mass of Water Lost[a] During Slaking	67	55	69
Net Increase in Mass[b] of Material Upon Slaking	376	385	374

[a] Corresponds to 15% (LIF-1), 13% (LIF-2), and 16% (LIF-3) of water lost during slaking.

[b] Corresponds to 37.6% (LIF-1), 38.5% (LIF-2), and 37.4% (LIF-3) of net increase in mass of waste material upon slaking.

TABLE 3.2

MEASURED AND CALCULATED ΔH VALUES FOR THE TEST MATERIALS

	Heat of Reaction (ΔH, cal/g)		
	LIF-1	LIF-2	LIF-3
Measured	-63	-64	-69
Calculated	-80.6	-78.4	-81.4

Knowing the CaO content of the test materials, we have calculated the heat of reaction for the three test samples (Table 3.2). As expected, LIF-1 and LIF-2, both based on the limestone injection process, exhibit almost identical heats of reaction. On the other hand, LIF-3, a reaction by-product of the lime injection process, has a much higher heat of reaction.

Considering that a 100% pure free lime sample has a heat of reaction of -278 cal/g, the above results indicate the presence of substantial amounts of non-exothermic materials (fly ash, calcite, anhydrite, etc) in the LIF waste by-product.

As evident from Table 3.2, the measured values are found to be consistently lower than the calculated values. However, this discrepancy is usually less than 15% and may be related to the ettringite formation reaction which was not considered in our calculations.

3.2 Chemical and Mineralogical Composition

The "as received" test materials (LIF-1, LIF-2, LIF-3) were analyzed for their major, minor, and trace constituents using thermal neutron activation analysis, atomic absorption spectroscopy, and wet chemical analysis.

The chemical composition of the three waste materials is presented in Tables 3.3 and 3.4. The major elements are reported as oxides. Since the silica values (SiO_2) are not available at this time, the totals of the major element oxides do not add up to 100%. However, LIF-2 was also analyzed for the major components by X-ray fluorescence analysis. The results show that SiO_2 is one of the major constituents of the LIF waste by-product, indicating that the discrepancy observed in the major element composition (Table 3.3) is attributable to the silica content.

The trace element composition, shown in Table 3.4, indicates the presence of a whole range of elements with As, Rb, Ba, Sr, Cr, and V at the ten to 100 parts per million level, while U, Se, Co, and Sb are present in the <10 ppm concentration range.

The mineralogy of the test materials was determined by X-ray diffraction analysis. For the "as received" test material, the X-ray diffraction peak intensities of the major crystalline phases present in the three samples are given in Table 3.5. The principal mineralogical phases are free lime (CaO), anhydrite ($CaSO_4$), calcite ($CaCO_3$), and quartz (SiO_2), with minor amounts of magnetite (Fe_3O_4) and mullite ($Al_6Si_2O_{13}$). A distinct hump observed at 23.5° 2θ on the X-ray diffractogram is indicative of the presence of amorphous material, most likely amorphous silica associated with fly ash in LIF waste by-products. Quartz, mullite, magnetite, and amorphous silica represent the major components of fly ash, whereas free lime and calcite represent unreacted feed material. Anhydrite is an end-product of the FGD reaction process. Relative to LIF-1 and LIF-2, LIF-3 exhibits a higher lime content and depletion in calcite. This can be attributed to the fact that LIF-1 is

TABLE 3.3

MAJOR ELEMENT COMPOSITION OF LIF WASTE

Major Elements	Concentration (%) LIF-1	LIF-2	LIF-3	NBS Fly Ash[a]
Al_2O_3	9.26	11.90	11.33	21.91
CaO	39.06	33.60	38.78	5.99
Fe_2O_3	8.56	12.29	7.45	b
K_2O	0.84	1.21	0.96	2.12
MgO	3.36	1.09	0.49	3.04
Na_2O	0.31	0.36	0.35	0.44
SiO_2	b	b	b	b
TiO_2	0.42	0.55	0.53	1.03
CO_2 (Carbonate)	5.94	4.20	2.89	b
SO_3 (Sulphate)	6.58	5.13	5.77	b
Unburnt Carbon	3.70	3.24	1.96	b
Total	78.03	73.57	70.52	34.53

[a] National Bureau of Standards (NBS) reference fly ash No. 1633 was used as a standard for neutron activation analysis.

[b] Not determined.

TABLE 3.4

TRACE ELEMENT COMPOSITION OF LIF WASTE

Trace Elements	Concentration (mg/L)			
	LIF-1	LIF-2	LIF-3	NBS Fly Ash[a]
As	49	58	36	b
Ba	370	530	450	3,175
Co	2.3	3.0	2.4	b
Cr	83	112	87	b
Cs	5.0	3.5	a	b
Mn	140	140	160	491
Rb	30	47	44	b
Sb	2.7	1.1	2.4	b
Sr	750	840	830	1,600
Se	7	6	11	b
U	7	8	8	14
V	130	130	110	217

[a] National Bureau of Standards (NBS) reference fly ash no. 1633 was used as a standard for neutron activation analysis.

[b] Not determined.

TABLE 3.5

X-RAY DIFFRACTION PEAK INTENSITIES OF MINERAL PHASES PRESENT IN THE "AS RECEIVED" LIF TEST SAMPLES [a]

	Peak Intensity (Counts/min)		
Mineral Phase	LIF-1	LIF-2	LIF-3
Free Lime (CaO)	1200	1200	1760
Anhydrite ($CaSO_4$)	350	250	360
Calcite ($CaCO_3$)	300	200	100
Quartz (SiO_2)	200	220	240
Magnetite (Fe_3O_4)	90	130	100
Mullite ($Al_6Si_2O_{13}$)	80	90	100

[a] Data provided by R.D. Hooton.

generated based on the lime injection process, whereas both LIF-2 and LIF-3 are a result of limestone injection.

Slaked samples, however, exhibit a different mineralogy, with portlandite ($Ca(OH)_2$), calcite, quartz, and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$) being the predominant phases. Minor amounts of mullite and magnetite are also present.

The X-ray diffractograms of LIF-2, before and after slaking, are displayed in Figure 3.1. Upon reaction with water, almost all of the free lime and anhydrite present in the sample are transformed into portlandite and ettringite, respectively.

There are basically two main reactions involved in the slaking process:

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (1)$$

and

$$3CaSO_4 + Al_2O_3 + 3Ca(OH)_2 + 29H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O \qquad (2)$$

A quantitative account of the observed changes in the mineralogy of LIF-2, upon slaking, is presented in Table 3.6. It is quite evident from Table 3.6 that the free lime in the "as received" LIF sample is the most reactive chemically in that all of it, upon reaction with water, is transformed into portlandite and ettringite. Calcite, amorphous and crystalline silica, magnetite, and elemental carbon exhibit practically no reactivity upon slaking. All of anhydrite, a part of mullite and free lime react to form ettringite in the slaked sample.

Scanning electron microscopic analysis of the "as received" test materials reveals the presence of three main phases, exhibiting distinct habits and morphologies (Figure 3.2): platy anhydrite, clumpy lime, and spherulitic fly ash. Energy dispersive X-ray analysis further reveals that most of the fly ash spherules are silliceous, with iron-rich, metallic spherules being less abundant.

4.0 FGD WASTE LEACHING BEHAVIOUR

Leaching tests were performed on LIF test samples to define the geochemistry of the leachates generated and to evaluate the source term for the FGD waste. This information is needed to assess the impact of FGD waste disposal on the environment and to identify suitable liner materials for use at an FGD waste disposal site.

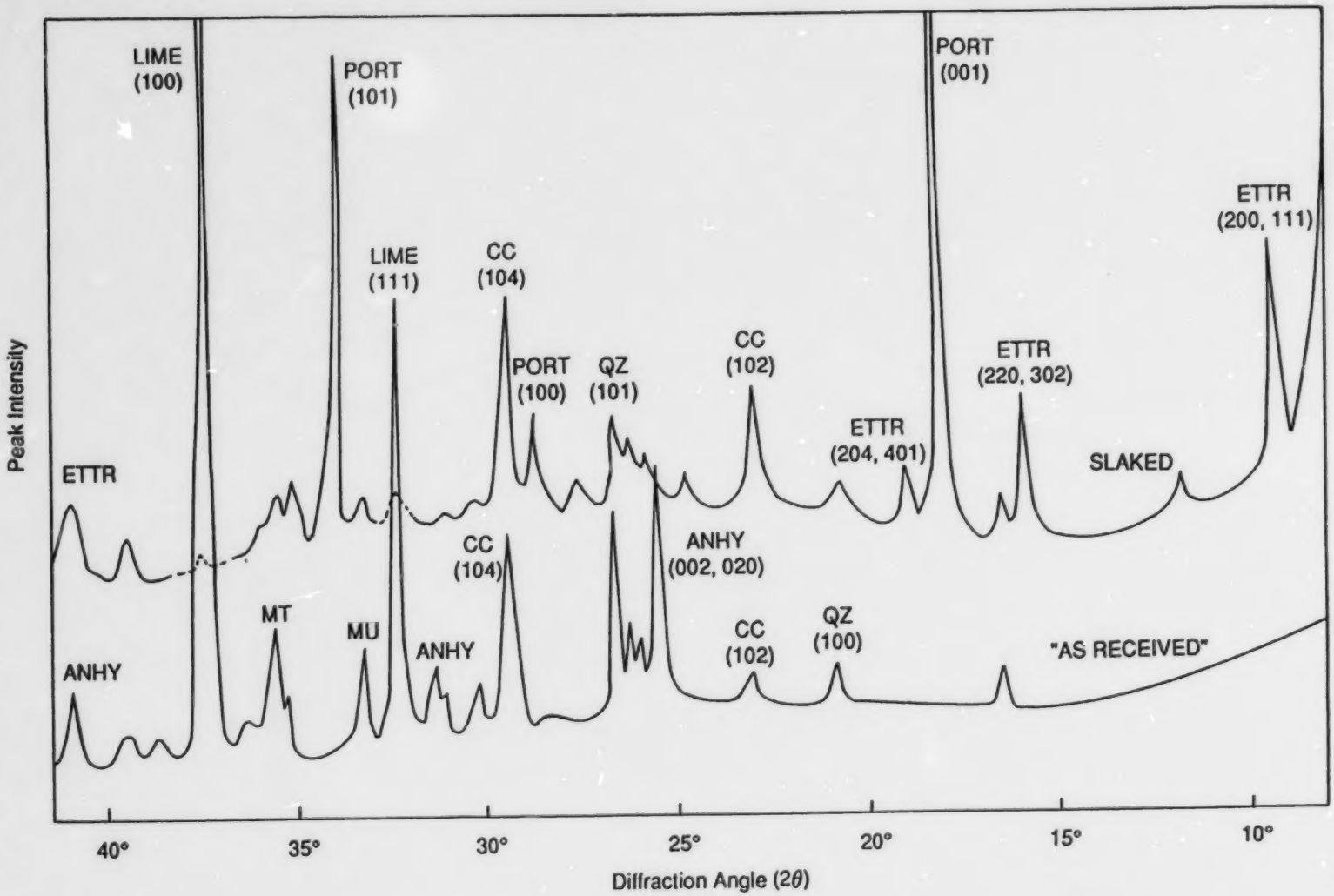


Fig. 3.1. X-ray diffractograms of the "as received" and slaked LIF-2 test sample, showing changes in bulk mineralogy upon slaking.

TABLE 3.6

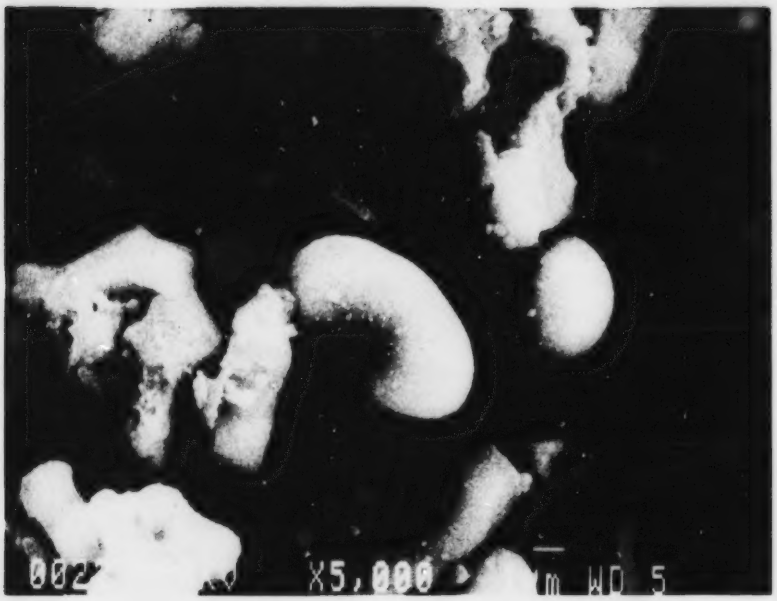
QUANTITATIVE MINERALOGY OF LIF-2 SAMPLE, BEFORE AND AFTER SLAKING[a]

	"As Received"	Slaked
Quicklime	30.2	[b]
Portlandite	[b]	22.8
Calcite	9.5	9.1
Anhydrite	9.6	[b]
Ettringite	[b]	25.8
Silica (amorphous & quartz)	18.9	17.0
Mullite[c]	18.5	12.7
Magnetite	10.1	8.7
Refractory Carbon	3.1	2.7
Total	99.9	98.8

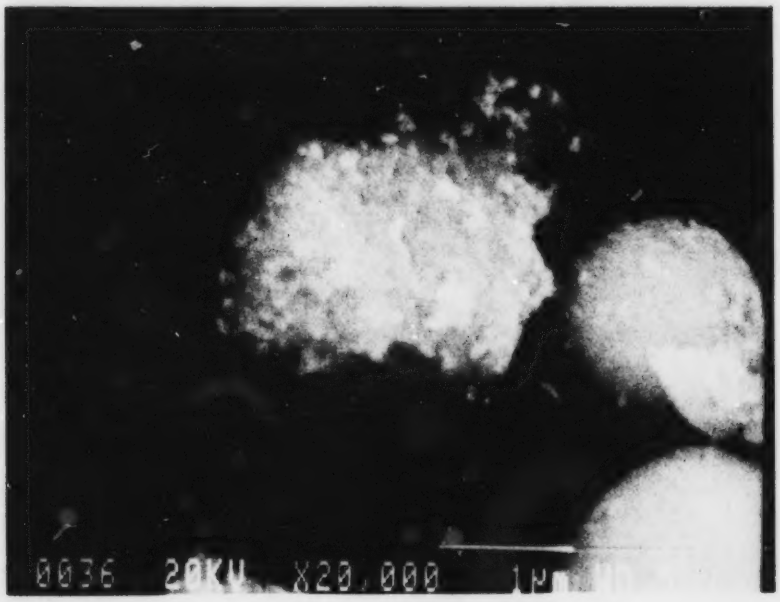
[a] Calculated based on X-ray diffraction, X-ray fluorescence, and wet chemical analysis of LIF-2, before and after slaking.

[b] Not detected.

[c] All alumina in the "as received" sample is assumed to be present in mullite.



(a)



(b)

FIGURE 3.2

Electron micrographs of the "as received" LIF waste sample (a) platy anhydrite and spherulitic fly ash; (b) clumpy free lime.

4.1 MOE Leachate Extraction Procedure

The MOE Leachate Extraction Procedure is the regulatory extraction test used in the province of Ontario. This test is based on the Extraction Procedure Toxicity Test (EP TOX) promulgated by the U.S. Environmental Protection Agency in 1980 to classify wastes as either hazardous or non-hazardous, based on a 95% municipal 15% industrial co-disposal scenario for inorganic wastes (Cote et al., 1988).

As described by Chan et al. (1988), the MOE leachate extraction tests have been completed on the three LIF test samples. Briefly, the test involves the leaching of a crushed sample in deionized water (solid: water = 1:20, on a weight basis) under continuous tumbling action for a period of 24 hours. Following completion of the leach tests, the leachates are filtered using a 0.45 μm millipore filter.

The leach data for the three test samples are presented in Table 4.1. For comparison purposes, leach data for a Lakeview fly ash sample is also presented. Compared to the maximum permissible concentrations of contaminants for hazardous waste categorization (Ministry of the Environment, 1983), it appears that the LIF leachates meet the regulatory guidelines, indicating that the FGD waste, based on the LIF process, can be categorized as non-hazardous.

4.2 Static Equilibrium Leaching Test

Although the MOE leachate extraction test is relevant to the regulatory requirements for the classification and categorization of hazardous waste, it does not provide kinetic information on the leaching behaviour of FGD waste and on the underlying processes controlling waste leaching. Furthermore, the 24-hour leaching period does not necessarily generate maximum concentrations as specified in Regulation 309 for hazardous waste.

With this in mind, static leaching tests were performed on the LIF-2 test sample to: (a) derive kinetic data on waste leaching; (b) obtain maximum solubility-limiting leachate concentrations; (c) generate leachate data amenable to geochemical modelling; and (d) obtain source term data on the FGD waste for evaluation and selection of suitable clay liner materials for use at a FGD waste disposal site.

Briefly, the leaching test involves using a crushed sample (5g), which is allowed to react with 50 ml of deionized water for a pre-determined length of time. A battery of leaching tests was initiated at the same time (same solid/liquid ratio in all cases), but allowed to continue for varying periods of time to obtain kinetic information on the leaching behaviour. Following completion of a leaching test at the pre-determined time, corresponding to a discrete kinetic data point, the leachate is separated from the solid and analyzed for the major dissolved constituents.

To date, five sets of leaching tests have been completed, corresponding to a total elapsed leach time of 14 days. The next set of on-going tests will be

TABLE 4.1

LEACHATE COMPOSITION OF LIF WASTE AND LAKEVIEW FLY ASH[a,b,c]

Contaminant	Lakeview Fly Ash	LIF-1	LIF-2	LIF-3	Leachate Quality Criteria[d]
Ag	<0.0001	<0.0005	<0.0005	<0.0005	5
As	0.03-0.04	<0.001	<0.001	<0.001	5
Ba	0.5-0.9	2.6	2.6	2.0	100
B	4.9-9.6	5.15	5.12	2.47	500
Cd	e	<0.0002	<0.0002	<0.0002	0.5
Cl^-	4-16	57.0	46.4	46.4	f
Cr	0.14-0.22	0.1	0.1	0.1	5
Cu	<0.0001	<0.1	<0.1	<0.1	f
F^-	e	1.24	1.49	1.46	240
Fe(T)	<0.05	<0.1	<0.1	<0.1	f
Hg	e	<0.0002	<0.0002	<0.0002	0.1
NO_3^- (as N)	0.01-0.34	0.23	0.11	0.14	1000
NO_2 (as N)	e	0.003	0.003	0.006	100
TOTAL N	e	0.233	0.113	0.146	1000
Ra-226	3	c	c	c	300
Se	0.03-0.16	0.012	0.014	0.009	1
SO_4^{2-}	515-986	1400	1240	1120	f
U	e	0.04	0.03	<0.02	2
CN^-	140.02	<0.02	<0.02	<0.02	20
PCB	0.0001	<0.001	<0.001	<0.001	0.3
pH	11-12	12.5	12.5	12.5	f

[a] Based on MOE leachate extraction procedure.

[b] All concentrations are reported as mg/L, except Ra-226(pCi/L).

[c] Adapted from Chan et al. (1988).

[d] Based on Regulations 309 for Hazardous Waste (Ministry of the Environment, 1985).

[e] Not determined.

[f] Not reported.

terminated after an elapsed leach time of 28 days.

The preliminary results of the leaching tests are presented in Table 4.2, indicating that the FGD waste leachates are highly alkaline (pH>12) and that the dissolved calcium and sulphate concentrations are orders of magnitude greater than the other dissolved constituents (K^+, Na^+, Cl^-, and dissolved inorganic carbon). At pH $\simeq$ 12, practically all of the dissolved inorganic carbon is present as CO_3^{2-}. Dissolved Al, Si, Mg^{2+}, and Fe_T are found to be below their analytical detection levels. The immeasurably low concentrations of Si, Fe, and Al are most likely a result of the slow dissolution kinetics of magnetite, silica, and mullite in the fly ash present in the LIF waste by-product.

As illustrated in Figure 4.1, both calcium and sulphate exhibit a steady decrease with increasing length of elapsed leach time. A similar trend has been observed by Constable et al (1988) for the leaching behaviour of calcium and sulphate in FGD waste derived from other sources.

5.0 GEOCHEMICAL MODELLING

In an earlier report (Dayal and Zhou, 1988), the authors demonstrated and evaluated the wide applicability of the geochemical computer program PHREEQE to diverse geochemical systems, in particular, the evaluation of FGD waste leaching and leachate/clay liner interactions as related to FGD waste disposal.

As discussed, in the case of FGD waste dissolution, PHREEQE can simulate the evolution of leachate chemistry with elapsed leach time and, at the same time, predict the mineral phases that are likely to exert control on the evolving leachate chemistry. Using the FGD waste dissolution data reported by Constable et al (1988), it was shown in an earlier report (Dayal and Zhou, 1988) that the FGD leaching behaviour can be predicted, with solid phases exerting a strong control on the evolving leachate chemistry.

In this report, inverse geochemical modelling was used to evaluate the results of the LIF-2 leaching tests presented in Table 4.2. The saturation states of the leachates in terms of the relevant mineral phases are presented in Table 5.1. The temporal changes in mineral saturation indices reflecting the evolving leachate chemistry with increasing length of the elapsed leach time are displayed in Figure 5.1.

The modelling results indicate that the leachates exhibit saturation with respect to portlandite, implying this phase could be controlling the leachate calcium concentrations. The leachate pH data also indicate portlandite to be the controlling phase. Gross oversaturation with respect to calcite and undersaturation with respect to gypsum and anhydrite indicate a lack of control of these phases on the evolving leachate chemistry. Since both gypsum and anhydrite exhibit gross undersaturation, the observed leachate sulphate concentrations may be limited by ettringite solubility. In fact, X-ray

TABLE 4.2

CHEMICAL COMPOSITION OF LIF-2 WASTE LEACHATES

Elapsed Leach Time (day)	pH	Conductivity (μmho/cm)	Concentration (mg/L)							
			Ca^{2+}	K^+	Na^+	SO_4^{2-}	DIC	Si	Al	Fe_T
1	12.4	a	914	39	21	560	3.6	<1	<0.5	<0.05
2	12.4	8350	918	40	20	585	4.6	<1	<0.5	<0.05
4	12.4	8275	896	44	20	508	5.6	<1	<0.5	<0.05
7	12.4	8375	845	48	24	362	4.1	<1	<0.5	<0.05
14	12.4	8450	703	59	27	164	3.0	<1	<0.5	<0.05

[a] Not determined.

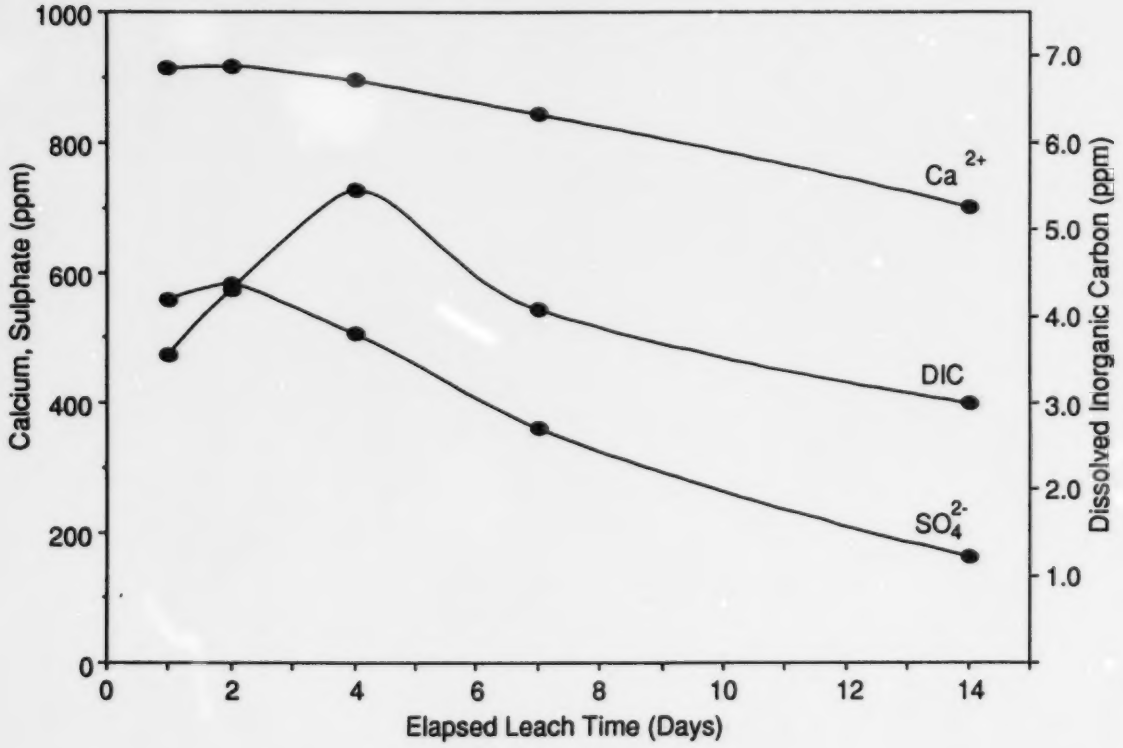


Fig. 4.1. Calcium, sulphate, and dissolved inorganic carbon concentrations in FGD waste leachates as a function of elapsed leach time.

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TABLE 5.1

MINERAL SATURATION INDICES OF LIF LEACHATES

Elapsed Leach Time (Day)	Saturation Indices (log IAP/KT)			
	Calcite	Portlandite	Gypsum	Anhydrite
1	1.73	0.10	-0.43	-0.65
2	1.83	0.08	-0.41	-0.63
4	1.92	0.09	-0.47	-0.70
7	1.78	0.11	-0.62	-0.85
14	1.64	0.02	-0.98	-1.21

diffraction data indicate the presence of ettringite in the slaked LIF sample. At this point, the thermodynamic data for ettringite is not available for inclusion in the PHREEQE data base.

Further modelling was performed to evaluate the interactions between FGD waste leachate and clay minerals to identify liner materials that are compatible with the alkaline FGD waste leachate. The interactions between the FGD waste leachate and liner materials can be evaluated using PHREEQE, provided the leachate chemistry is known. As a starting point, the saturation indices was calculated for the common rock-forming minerals and clay minerals. For this simulation, the 14-day leach data was assumed to represent steady-state equilibrium concentrations. For the purposes of modelling, 0.1 ppm of Al, Mg, Si, and Fe were added to the leachate system, which is assumed to be both closed and opened to the atmosphere ($pCO_2 = 10^{-3.5}$; $pO_2 = 10^{-0.7}$).

The modelling results are shown in Table 5.2. When closed to atmospheric CO_2 and O_2, the FGD leachates are undersaturated, relative to the major rock-forming minerals (quartz, plagioclase, orthoclase, etc.) and Al-rich clay minerals (kaolinite, gibbsite, muscovite, illite, montmorillonite). This is reasonable because the leachate is highly alkaline and both Si and Al will be susceptible to chemical attack. Therefore, the common rock-forming minerals and some clay minerals are not stable and may undergo slow dissolution upon

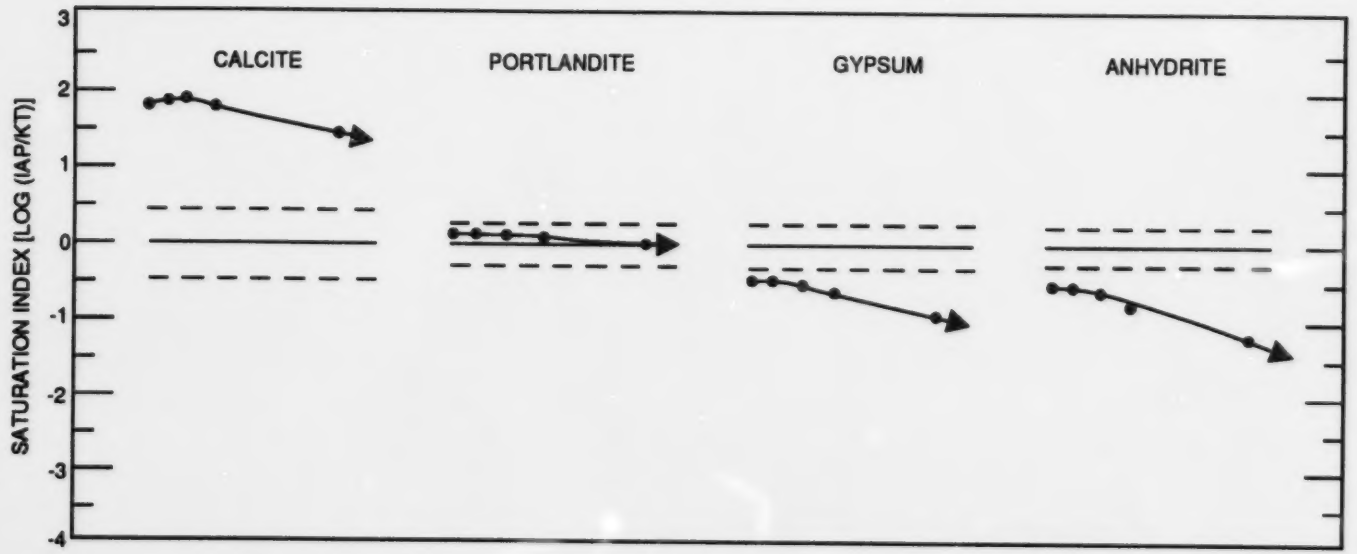

Fig. 5.1. Temporal changes in mineral saturation indices reflecting the evolving leachate chemistry with increasing length of elapsed leach time (indicated by arrows).

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TABLE 5.2

SATURATION INDICES FOR MAJOR ROCK-FORMING AND CLAY MINERALS RELATIVE TO LIF WASTE LEACHATE[a]

	SATURATION INDEX (LOG IAP/KT)	
	Closed to Atmosphere	Open to Atmosphere
Quartz	- 4.95	- 1.54
Kaolinite	-13.42	- 0.47
Gibbsite	- 2.50	0.13
Albite	-14.98	- 4.73
Anorthite	-10.58	- 3.06
Microcline	-12.90	- 2.64
Muscovite	-15.03	1.35
Illite	-21.40	- 5.68
Montmorillonite	-25.78	- 7.18
Na-Nontronite	- 6.77	11.86
Ca-Nontronite	0.29	18.89
Mg-Nontronite	- 0.67	17.99

[a] 14-day leach data was assumed to represent equilibrium leachate concentrations.

contact with alkaline waste leachates. On the other hand, the FGD leachates are oversaturated relative to Fe- and Mg-rich clays (chlorites, nontronites, and saponite) and these could serve as suitable liner materials at a waste disposal site, keeping in mind that the PHREEQE simulations of leachate/clay liner interactions are based on limited thermodynamic data base for the clay minerals.

When the FGD leachate reacts with atmospheric CO_2 and O_2, the solution pH decreases by 3 units. The decrease in pH is due to an increase in the dissolved CO_2 in the solution. As a result of such a change, the solution becomes saturated with almost all of the rock-forming minerals and clay minerals. The conclusion, of course, is based on the assumption that the 14-day leach data represents equilibrium leachate concentrations and assuming equilibrium with atmospheric CO_2 and O_2. The computer simulation of the FGD waste leaching behaviour and leachate/clay liner interactions can be validated by comparing it with the actual field data from a FGD disposal site.

6.0 CONCLUSIONS

A laboratory study was undertaken to define and evaluate the properties of flue gas desulphurization (FGD) waste by-products in terms of their chemical characteristics, leaching behaviour, and leachate interactions with clay liner materials. Specifically, the test materials used in this study are based on the limestone/lime injection into the furnace (LIF) process evaluation test runs carried out at Lakeview TGS.

Upon slaking, the LIF test materials exhibit exothermicity with the measured heats of reaction ranging from -63 to -69 cal/g, compared to a value of -278 cal/g for a 100% free lime sample.

The major constituents of LIF waste by-products are calcium oxide and silica, followed by alumina, iron oxide, sulphate, carbonate, unburnt carbon, and magnesium oxide.

The principal mineralogical phases present in the "as received" LIF material are free lime, anhydrite, calcite, and quartz, with minor amounts of magnetite and mullite. The latter four phases represent the major components of fly ash, whereas free lime and calcite represent unreacted feed material. Anhydrite is an end-product of the FGD reaction process.

Upon reaction with water, all free lime and anhydrite, along with a part of mullite, are transformed into portlandite and ettringite. Calcite, silica, magnetite, and elemental carbon exhibit practically no reactivity upon slaking.

Based on the MOE regulatory leach test, the results indicate that the FGD waste by-product can be categorized as non-hazardous.

Static equilibrium leach test results indicate that the FGD waste leachates are highly alkaline, with calcium and sulphate being the major dissolved constituents. K^+, Na^+, Cl^-, and dissolved inorganic carbon are also present, but exhibit orders of magnitude lower concentrations than Ca^{2+} and SO_4^{2-}.

The geochemical modelling results indicate the FGD leachates exhibit saturation with respect to portlandite. Since both gypsum and anhydrite exhibit gross undersaturation, it appears that the leachate sulphate concentrations may be controlled by another sulphate mineral phase such as ettringite.

The modelling results of FGD waste leachate/clay liner interactions indicate that Fe- and Mg-rich clays may serve as suitable liner materials at an FGD waste disposal site.

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REFERENCES

Chan, H.T., Johnston, H.M., Konecny, L., Hooton, R.D., and Dayal, R., 1988. Use of a Flue-Gas Desulphurization By-Product for Stabilizing Hydraulic Mine Backfill (in preparation).

Dayal, R., and Zhou, Z., 1988. Geochemical Modelling Relevant to Ontario Hydro's Waste Disposal Programs. Ontario Hydro Research Report No. 88-317-K, 34p.

Cote, P., Constable, T., Stegemann, J., Dayal, R., Sawell, S., Caldwell, R., and McLellan, J., 1989. Guide for the Selection of Leaching Tests. Wastewater Technology Centre, Environment Canada, 54p.

Golomb, A., 1988. FGD Waste Characterization/Disposal Study. Ontario Hydro Research Report No. 87-158-K, 67p.

Ministry of the Environment 1985. Regulation 309 - Revised Regulations of Ontario under Environmental Protection Act (General - Waste Management).

Mozes, M.S., Mangal, R., Thampi, R., and Tubman, D., 1988. Sorbent Injection for SO_2 Control. Ontario Hydro Research Report No. 88-63-K, 44p.